Shale Weathering in a Mountainous Watershed: Impact of Water Table Fluctuations and Implications for Nitrogen Cycling

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Abstract:

Shale formations represent critical contributors to global nitrogen and carbon cycles due to their widespread occurrence and high content of organic matter and carbonate minerals. In particular, shale bedrock weathering strongly influences the export of solutes and nutrients to rivers, leading to significant release of greenhouse gasses to the atmosphere. Understanding the complex interplay between hydrochemical, biogeochemical, and physical processes that control the transformation of shale bedrock represents a major scientific challenge for the interpretation of seasonal and longer-term cycling of nutrients.

In this study, we develop a modeling approach to quantitatively interpret long-term alteration of shale bedrock and analyze the coupling between shale weathering, seasonal water fluctuation, and the cycles of carbon and nitrogen along a well-instrumented hillslope-to-floodplain transect located in the East River Watershed. The model simulates the exchange of gasses between the atmosphere and the subsurface, the infiltration of meteoric water, a series of microbially-mediated reactions, including the cycling of nitrogen, as well as the transformation of mineral assemblages induced by dissolution/precipitation reactions.

The model results show that the ingress of oxygen drives the dissolution of sulfide minerals and a variety of microbially-mediated reactions. The degradation of organic matter enhances the dissolution of carbonate minerals and leads to significant emission of CO_2 into the atmosphere. In particular, the model indicates that modern organic matter is the primary source of nitrogen due to its relatively high reactivity although fossil shale-associated organic matter and atmospheric N deposition represent important secondary sources. While a large part of the nitrogen denitrifies in the unsaturated zone, dissimilatory nitrate reduction to ammonium represents an important nitrogen retention pathway in the saturated-anoxic zone. The degree of water saturation exerts a

strong control on the gas fluxes, and thus ultimately determines the weathering rates. In particular, the model shows that while the thickness of the weathered front is determined by the greatest depth of the water table, strong water table fluctuations occurring between dry and snow-melt periods result in rapid seasonal shifts in microbially-mediated reactions, mineral dissolution, and nutrients concentrations. On a longer time scale, these water table fluctuations can result in significant changes in the growth and activity of plant types. During low snow years, modeling results highlight the importance of deeper water, and potentially shale-derived nitrogen resources, in preferentially sustaining deep-rooted shrubs over shallow-rooted forbs at mid-slope locations. Finally, efforts are underway to understand how hillslope topography and floodplain retention may interact to impact hydrogeochemical exports to rivers under different snow years.